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A GAS-SOLID REACTION

Lutgard C. De Jonghe and Mei Chang

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**Abstract**

A method is developed defining the oxygen chemical potential on the surface of oxide on the metal phase during a gaseous reduction reaction. The method couples the gas reaction with a solid state defect reaction. It is shown that, during this gas/solid reaction, the surface oxygen chemical potential,  $\mu_s$ , is between that of the gas phase,  $\mu_g$ , and that of the metal/metal oxide equilibrium,  $\mu_e$ . If the adsorption-desorption step is slow,  $\mu_s$  is close to  $\mu_e$ ; if the adsorption-desorption step is fast,  $\mu_s$  is close to  $\mu_g$ .

## I. Introduction

In certain gas-solid reactions, such as oxide reduction by  $\text{CO}/\text{CO}_2$  mixtures, it may be necessary to define the surface oxygen chemical potential. This potential is an important quantity, since it provides a boundary value for solid state transport processes that occur as part of the reaction mechanism. The significance of this surface oxygen chemical potential was recently demonstrated by Chang and De Jonghe<sup>(1)</sup> for the gaseous reduction of an ion bearing oxide, cobalt ferrite, where the oxygen chemical potential at the metal-oxide-gas triple junction,  $\mu_s$ , determines the morphology of the metallic reaction product. In the case of  $\text{CO}/\text{CO}_2$  reduction of the cobalt ferrites, metallic alloy whiskers are formed, as shown in Fig. 1, with a diameter that is determined by the rate at which the oxygen is removed from under the whisker-the metal-oxide interface-and by a surface gas/solid reaction at triple junction. The situation is shown schematically in Fig. 2. This oxygen chemical potential is between that for the metal-oxide equilibrium,  $\mu_e$ , and that for the gas phase equilibrium,  $\mu_g$ . In this paper we considered how the oxygen chemical potential,  $\mu_s$ , may be defined for a reduction reaction when the oxide or the metal surface is the active reaction phase where the conversion of  $\text{CO}$  to  $\text{CO}_2$  occurs.

## II. Kinetic and Thermodynamic Consideration

Only the simplest reaction sequence will be considered here. This will permit a clearer discussion of the procedure, without undue algebraic complexity.

During a gas-solid reaction, such as reduction of oxide, MO, to metal, M, by CO/CO<sub>2</sub>, the oxygen chemical potential in the gas phase,  $\mu_g$ , will differ from the one on the surface of the solid,  $\mu_s$ , which in turn will differ from the MO/M equilibrium one,  $\mu_e$ . The reduction reaction may, in its most elementary form, be described by a first order reaction sequence:



This sequence does not specify where the adsorption, exchange, or desorption reactions occur. In actuality, different parts of the reactions may well take place on different phases when both metal and oxide are present as surface phases; e.g., adsorption might occur on the metal surface, followed by surface diffusion of the reaction product to the adjacent oxide where desorption might occur easily, similar to processes occurring on bifunctional catalysts or in spill-over processes.<sup>(2,3)</sup>

These and other complications will, however, be ignored here. To define the oxygen chemical potential on the surface during reaction we first

find  $R_a = [\text{CO}(a)]/[\text{CO}_2(a)]$ . Equations (1) to (3) give the first order flux equations during steady state:

$$J = k_1[\text{CO}(g)] - l_1[\text{CO}(a)] \quad (4)$$

$$= k_2[\text{CO}(a)] - l_2[\text{CO}_2(a)] \quad (5)$$

$$= k_3[\text{CO}_2(a)] - l_3[\text{CO}_2(g)] \quad (6)$$

which, after some algebra, leads to:

$$R_a = [R_g k_1 (k_3 + l_2) + l_2 l_3] / [R_g k_1 k_2 + l_3 (k_2 + l_1)] \quad (7)$$

One can also write:

$$J = k^*[\text{CO}(g)] - l^*[\text{CO}_2(g)] \quad (8)$$

where:

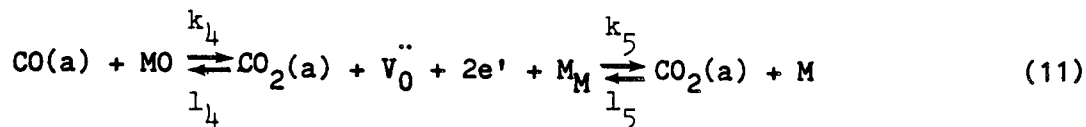
$$k^* = k_1 k_2 k_3 / (k_2 k_3 + k_3 l_1 + l_1 l_2) \quad (9)$$

and

$$l^* = l_1 l_2 l_3 / (k_2 k_3 + k_3 l_1 + l_1 l_2) \quad (10)$$

To find the oxygen chemical potential in the surface during reaction, a solid state interaction must be invoked. For gaseous reduction with the relevant reactions occurring on the oxide phase, oxygen is removed from the MO lattice so that, in the simplest case, using

Kröger-Vink rotation,<sup>(4)</sup> Reaction (2) and (3) is replaced by:



with the flux equations:

$$J = k_4[\text{CO(a)}] - l_4[\text{CO}_2\text{(a)}][\text{V}_0^{\bullet\bullet}][\text{e}']^2 \quad (12)$$

$$= k_5[\text{CO}_2\text{(a)}][\text{V}_0^{\bullet\bullet}][\text{e}']^2 - l_5[\text{CO}_2\text{(a)}] \quad (13)$$

These two reactions can be combined and put in the same form as Eq. (5), giving a new expression for  $k_2$  and  $l_2$ :

$$k_2 = k_4 k_5 / (k_5 + l_4) \quad (14)$$

$$l_2 = l_4 l_5 / (k_5 + l_4)$$

With these substitutions, the expression for  $R_a$ , Eq. (7), retains the same form. Since the crystal defects, the oxygen vacancies  $\text{V}_0^{\bullet\bullet}$  and the electron  $\text{e}'$ , are occurring in the solid state, local equilibrium between them prevails, and one may write:



where  $K_6 = k_6/l_6$ , and where the  $p_{\text{O}_2}$  is an effective oxygen partial pressure that would have established the same non-stoichiometry in the surface as the one exposed by Eq. (11). From Eq. (15) it follows that:

$$[\text{V}_0^{\bullet\bullet}][\text{e}']^2 = K_6/p_{\text{O}_2}^{1/2} \quad (16)$$



Thus, combination of Eqs. (12) and (16) gives:

$$p_{O_2}^{1/2} = CO_2 \left[ \frac{(a)}{[CO(a)]} \right] \frac{K_6}{K_4} / (1 - J/k_4[CO(a)]) \quad (17)$$

Elimination of  $[CO(a)]$  with Eq. (7) and of  $J$  with Eq. (8) and with  $K_a = k_1/l_1$ , leads to:

$$p_{O_2}^{1/2} = \frac{K_5}{K_4} \frac{1}{R_a} / \left( 1 - \frac{\left( 1 - \frac{R_g^o}{R_g} \right)}{k_4 \left[ \frac{K_a}{k^*} - \left( 1 - \frac{R_a^o}{R_g} \right) / l_1 \right]} \right) \quad (18)$$

where  $R_g^o = l^*/k^*$ , the M/MO equilibrium  $CO(g)/CO_2(g)$  ratio in Eq. (8).

At equilibrium, combination of Eq. (11) and (15) also yields that

$$K_6/K_4 = R_a^o (p_{O_2}^o)^{1/2} \quad (19)$$

where  $R_a^o$  and  $p_{O_2}^o$  are the M/MO equilibrium values of  $R_a$  and  $p_{O_2}$ . The oxygen chemical potential in the surface during reaction will then be

$$\mu_s = \mu_s^o + kT \ln p_{O_2}^{1/2} \quad (20)$$

If we put

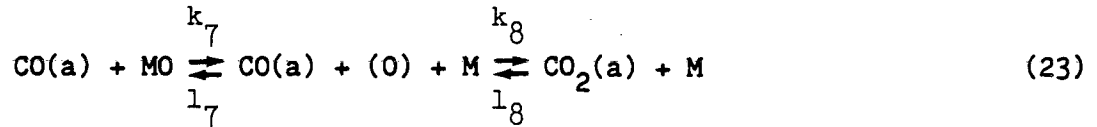
$$\Delta\mu_{MO} = \mu_s - \mu_e \quad (21)$$

then combination of Eqs. (18) through (21) gives

$$\mu_{MO} = kT \ln \left\{ \frac{R_a^O}{R_a} / \left( 1 - \frac{\left( 1 - \frac{R_g^O}{R_g} \right)}{k_4 \left[ K_a/k^* - \left( 1 - \frac{R_g^O}{R_g} \right) / l_1 \right]} \right) \right\} \quad (22)$$

If the gas-solid exchange process occurs on the metal phase M in an M-MO two phase surface, a different reaction scheme can be condensed.

Then, Eqs. (2) and (3) are replaced by:



where (O) is oxygen dissolved in the M surface. The (O) can again be considered to establish the surface oxygen chemical potential by:



The same procedure as before, with  $K_d = k_3/l_3$ , then leads to:

$$\mu_M = kT \ln \left\{ \frac{R_a^O}{R_a} \left( \frac{K_d \left( \frac{R_g}{R_g^O} - 1 \right)}{l_8 \left[ \left( \frac{R_g}{R_g^O} - 1 \right) / l_3 + 1/l^* \right]} + 1 \right) \right\} \quad (25)$$

with  $k_2$  and  $l_2$  in Eqs. (7) and (9) and (10) now replaced by

$$k_2 = k_7 k_8 / (l_7 + k_8) \quad (26)$$

$$l_2 = l_7 l_8 / (l_7 + k_8) \quad (27)$$

To predict how  $\mu_{MO}$  or  $\mu_M$  depends on reaction conditions would require knowledge of a large number of reaction rate parameters  $k_i$  and  $l_i$ . This information is rarely, if ever, available. It is, however, useful to consider the trend of  $\Delta\mu$  for limiting cases where the surface processes or the adsorption-desorption reactions are rate controlling. Such calculations have been performed for Figs. 3 and 4. Various values of  $k_i = l_i$  have been assumed for the case where  $R_g^0 = 1$ . Curve A in Figs. 3 and 4 give  $\Delta\mu$  as a function of  $R_g/R_a^0$ , for all  $k_i = l_i = 1$ . It is evident when exchange reactions are fast compared to adsorption-desorption reaction, case B in Figs. 3 and 4, that  $\mu_s$  remains close to  $\mu_e$ . When adsorption-desorption processes are fast compared to the surface exchange reactions, case C in Figs. 1 and 2,  $\mu_s$  remains closer to  $\mu_g$ . In this case, a larger driving force is available for the transporting oxygen from under the metal to the face surface, shown schematically in Fig. 1a.

### III. Conclusions

The surface oxygen chemical potential during a gas-solid reaction, such as the reduction of an oxide by CO/CO<sub>2</sub> gas mixtures, can be defined by invoking a solid state defect reaction. For the gaseous reduction of MO to M, this chemical potential is between that of the gas phase and that of the MO/M equilibrium, depending on the relative rates of adsorption-desorption and surface exchange reactions.

### IV. Acknowledgements

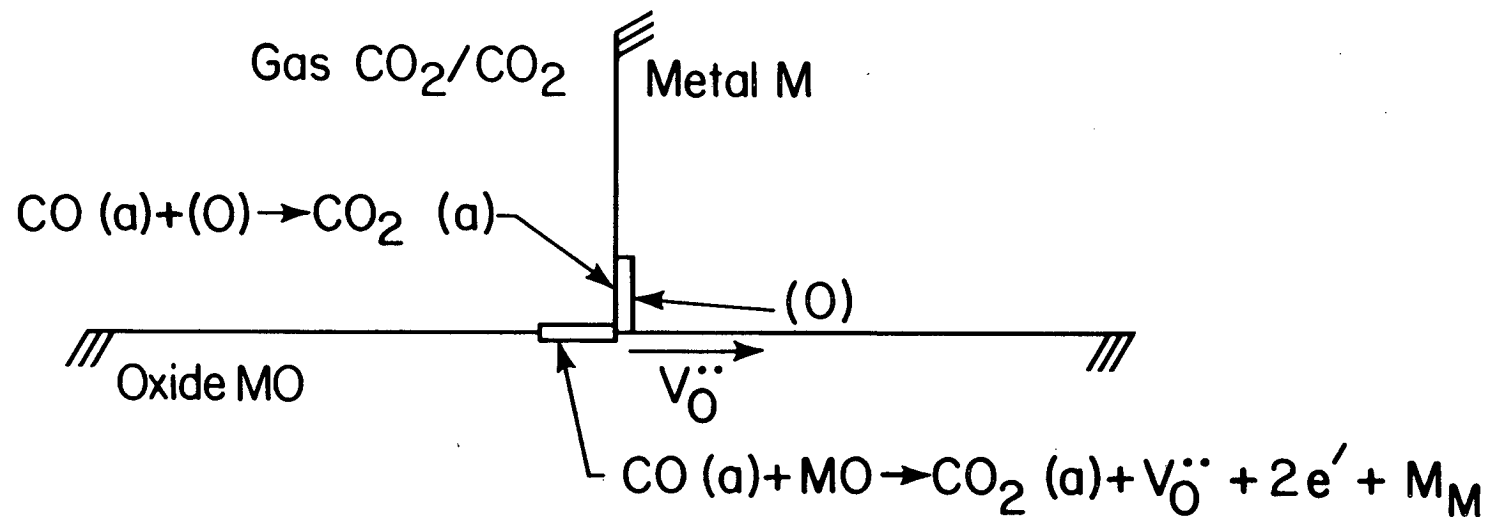
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2. G. C. Bond, and P. Sermon, J. Chem. Soc. Farad. Trans. I 76 (1980), 889.
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4. F. Kröger, "The Chemistry of Imperfect Crystals," North Holland, Amsterdam, 1974.

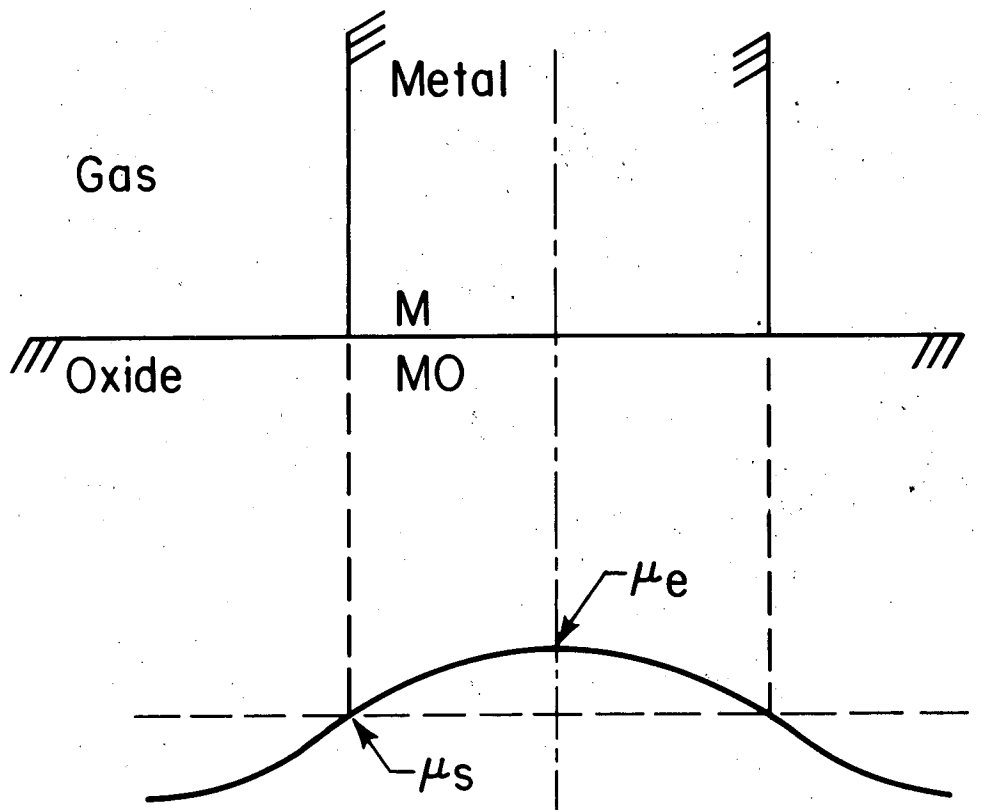
### Figure Captions

- Fig. 1. a) Reactions occurring on the metal or on the oxide phase near the metal-oxide-gas triple junction. Oxygen vacancies or dissolved oxygen may need to be transported along or near the metal-oxide interface when the progress of the reaction requires that oxygen is removed from that interface.
- b) Schematic representation of the oxygen chemical potential for a reduction reaction where oxide MO is converted to metal M.
- Fig. 2. Example of metal whiskers formed as a result of CO/CO<sub>2</sub> reduction of the oxide CoFe<sub>2</sub>O<sub>4</sub>. The oxide was reduced at 900°C, for 300 sec, at a total gas pressure of 100 torr, with CO/CO<sub>2</sub> = 11.8.
- Fig. 3.  $\mu_{MO}$  as a function of  $R_g/R_g^O$  for various assumed values of  $k_i$  and  $l_i$ , with  $R_g^O = 1$  and  $k_i = l_i$  for all cases.
- Fig. 4.  $\mu_M$  as a function of  $R_g/R_g^O$  for various assumed values at  $k_i$  and  $l_i$ , with  $R_g^O = 1$ , and  $k_i = l_i$  for all cases.



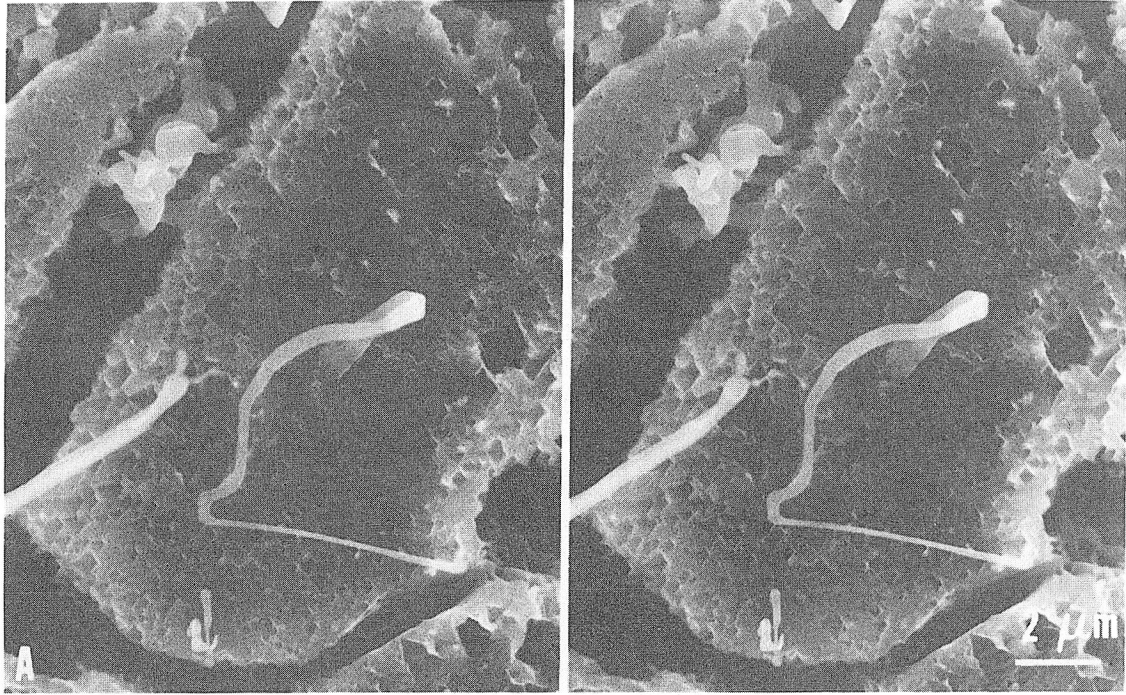
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Fig. 1a



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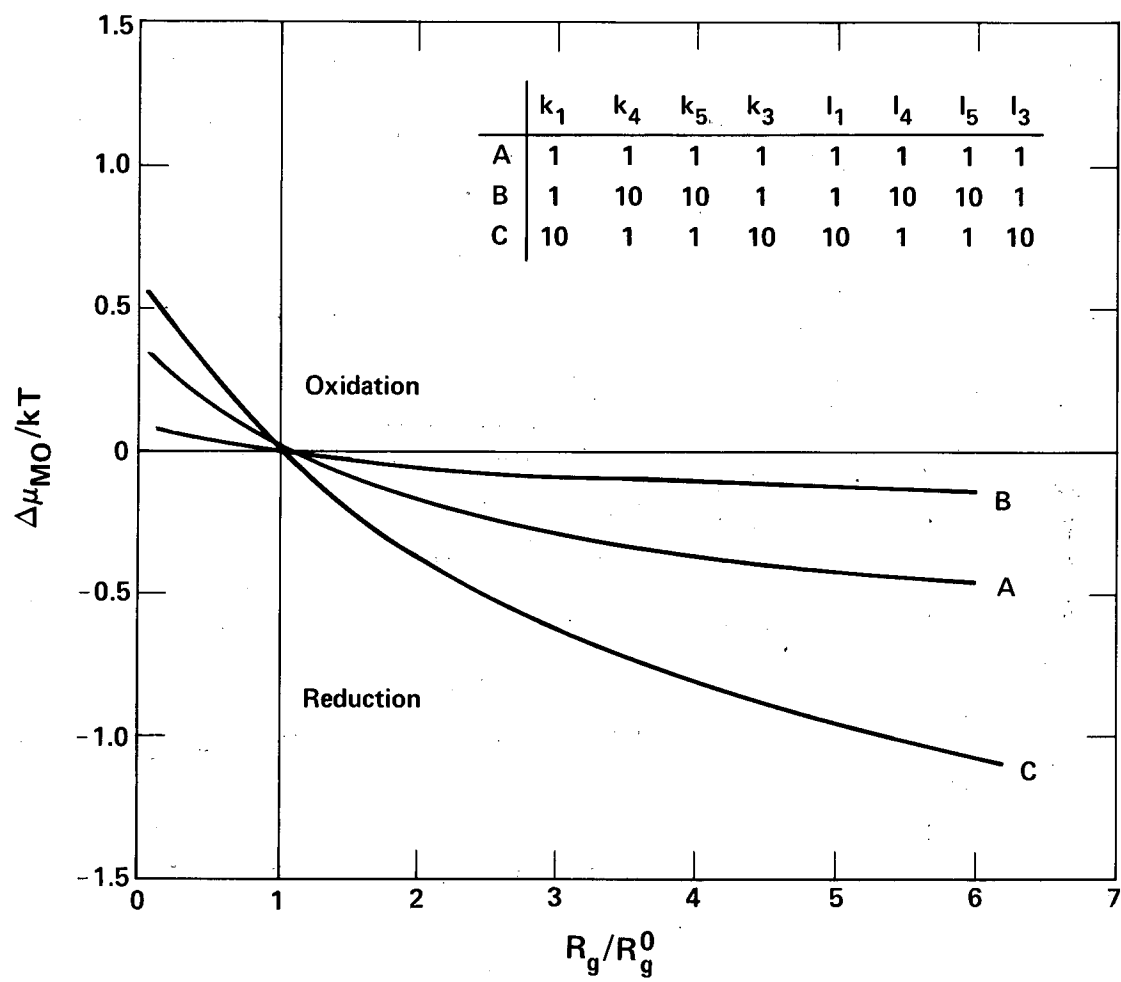
Fig. 1b



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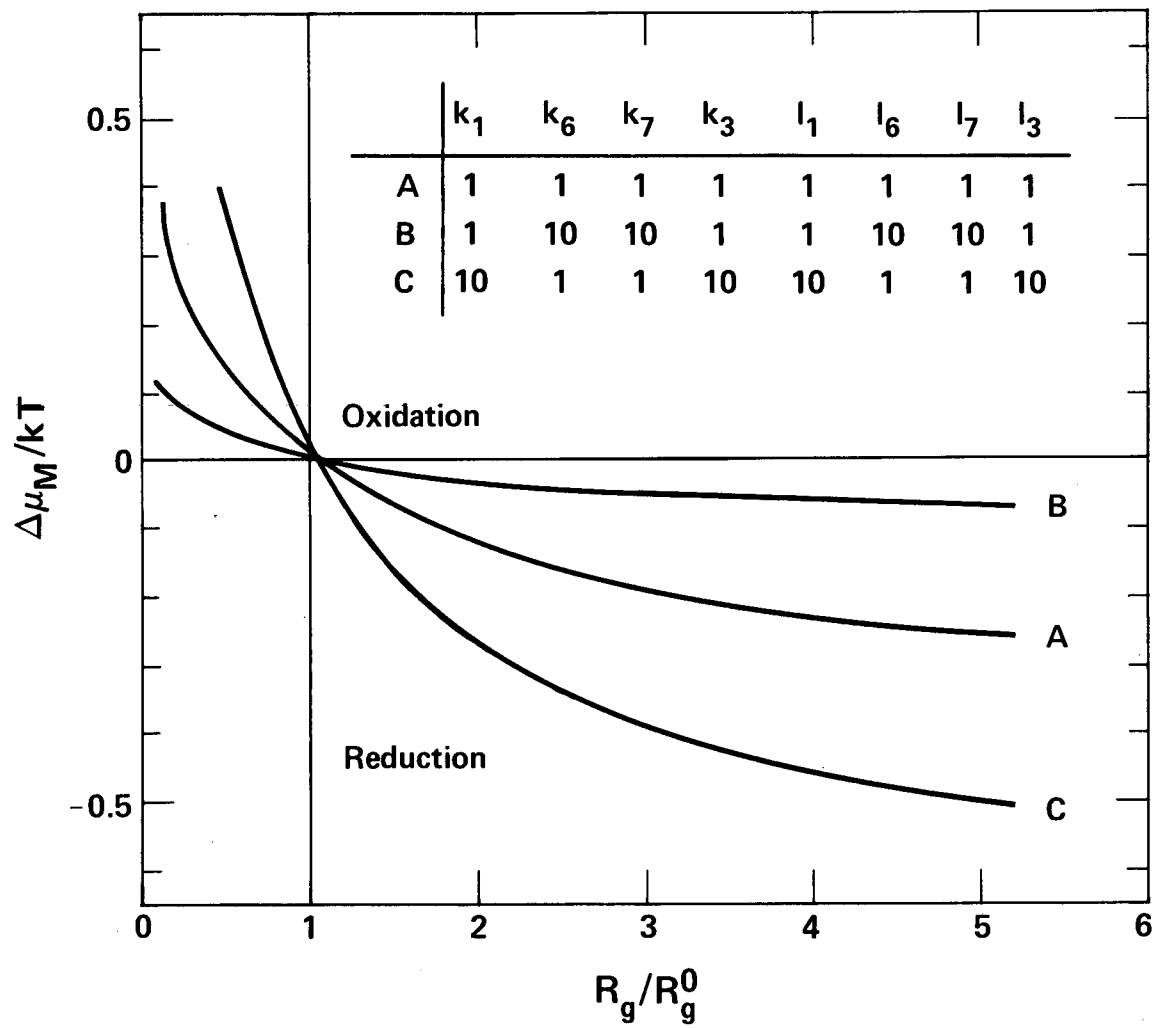
Fig. 2





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Fig. 3



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Fig. 4

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